BLOCK COPOLYMERS BY THE CONVERSION OF LIVING LITHIUM INITIATED ANIONIC POLYMERIZATION INTO LIVING RUTHENIUM ROMP

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ABSTRACT: This paper describes a method for the synthesis of well-defined AB block copolymers, where one block is synthesized via anionic polymerization initiated with alkyllithium compounds, and one by ring opening metathesis polymerization (ROMP) using well-defined ruthenium macroinitiators. This methodology was demonstrated by copolymerizing styrene with norbornene derivatives. Polystyrene was synthesized via living anionic polymerization initiated by *sec*-butyllithium, and functionalized to form macromonomers. These were used as precursors to well-defined ruthenium

macroinitiators, the macromonomers being converted by an alkylidene exchange reaction with ruthenium propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$. These macroinitiators were used to initiate the ROMP of various norbornene derivatives in order to synthesize well-defined block copolymers with narrow molecular weight distributions.

Introduction

Living polymerization techniques are powerful tools that allow the synthesis of polymers that are well-defined in terms of molecular weight and polydispersity.[1] Amongst these techniques are anionic polymerization[2,3] and ring opening metathesis polymerization (ROMP).[4-6] One of their applications is in the synthesis of block copolymers, most commonly by the sequential polymerization of monomers using a single living polymerization mechanism.[3] A more recently developed alternative to this methodology is the synthesis of block copolymers by the combination of two different living polymerization mechanisms.[7] The latter approach can be used to synthesize novel block copolymers containing polymeric blocks derived from monomers that can not be copolymerized by any single technique. We have recently reported a method for the synthesis of block copolymers using the combination of potassium initiated living anionic polymerization and living ROMP initiated by well-defined ruthenium initiators.[8] The anionically polymerized block was poly(ethylene oxide) (PEO), initiated by diphenylmethylpotassium. The potassium/oxyanion pairs of the living PEO produced by the polymerization reaction were reacted directly with 4-vinylbenzyl chloride (4-VBC), to yield macromonomers that were subsequently transformed into ROMP macroinitiators by an alkylidene exchange reaction with ruthenium propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$. However, the majority of anionic polymerization reactions (for example that of styrene) are typically initiated using alkyllithium compounds such as *sec*-butyllithium.[3] It is thus highly desirable to demonstrate that these polymerization reactions can be combined with ruthenium ROMP in order to extend the range of attainable block copolymers. These anionic polymerizations produce polymers with stable living chain ends consisting of a lithium/carbanion pair, which are available for functionalization. Unfortunately the

nucleophilicity of living polystyrene (PS) means that the direct end functionalization reaction of the living polystyrllithium with 4-VBC is accompanied by a side reaction between the active site on the PS and the vinyl group of the 4-VBC.[9]

This paper describes a modified strategy to convert polymers formed from living lithium initiated anionic polymerization into ruthenium macroinitiators for ROMP and their use in the synthesis of block copolymers. This is demonstrated by copolymerizing styrene with norbornene derivatives. Although there have been previous reports of block copolymers containing a block polymerized via ROMP initiated by well-defined molybdenum initiators, and a PS block polymerized via either an anionic,[10] or a radical[11] mechanism, the lower functional group tolerance of molybdenum ROMP initiators, in comparison to their ruthenium counterparts, limits the range of functionalities that can be incorporated into the ROMP block of the copolymers using these strategies.[4,12]. In a further investigation[13] block copolymers were prepared using a combination of ROMP and atom transfer radical polymerization (ATRP) using vinylic ethers as chain transfer agents but the resulting materials were not well defined. The methodology reported here should allow the synthesis of well-defined block copolymers of styrene, and other monomers that can be polymerized via an anionic mechanism, with norbornene monomers containing a wide range of functionalities.

Experimental Section

Materials. Styrene (Aldrich, 99+%) and benzene (Aldrich, 99.9+%) were distilled from CaH_2 prior to use. Ethylene oxide (EO, Aldrich, 99.5+%) was purified by distillation from CaH_2 and then by distillation from $Mg(Bu)_2$ (Aldrich, 1.0 M solution in heptane) immediately before use. 4-Vinylbenzyl chloride (4-VBC, Aldrich, 90%) contained the impurities, α-chloromethyl styrene (2%), dichloromethyl styrene (3%) and 3-vinylbenzyl chloride (3-VBC, 5%), and was purified as described later in the text. *sec*-Butyllithium (Aldrich, solution in hexane), potassium (Aldrich, 98%), 15-crown-5 (Aldrich, 98%) and ethyl vinyl ether (Aldrich, 99%) were used as supplied. Sodium hydride (Aldrich, dry, 95%) was stored and handled under nitrogen at all times. The preparation of the ROMP monomers and ruthenium propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ have been described previously.[8]

Anionic polymerizations were terminated using MeOH (Aldrich, 99.9+%) that had been sparged with N_2 for 30 min. THF (Aldrich, 99.9%, anhydrous) used for azeotropic distillation and as a solvent for Williamson coupling reactions was passed through two columns containing alumina.[14] Hexane (Aldrich, 95+%, anhydrous) used in the precipitation of the macroinitiator was degassed prior to use. CH_2Cl_2 (Aldrich, 99.9%) was distilled from CaH_2. CD_2Cl_2 (Goss/Cambridge Isotope Laboratories Inc., 99.9% D, 0.03% v/v TMS) and $CDCl_3$ (Aldrich, 99.9% D, 0.03% v/v TMS) were used as received. C_6D_6 (Aldrich, 99.6% D, 0.03% v/v TMS) was purified by distillation from CaH_2.

Analytical Measurements. Nuclear Magnetic Resonance (NMR) spectroscopy was performed using a Varian Inova-500 MHz or Mercury-400 MHz spectrometer. All ^1H and ^{13}C NMR resonances are quoted relative to TMS unless otherwise stated.

GPC was performed using a Viscotek 200 with refractive index, viscosity and right angle light scattering detectors and 2 x 300 mm PLgel 5 μm mixed C columns. THF was used as the eluent, at a flow rate of 1.0 mL/min and at a constant temperature of 30 °C. Molecular weights were obtained using triple detection. The detectors were calibrated with a single, narrow molecular weight distribution PS standard (M_w = 66 000 g mol^{-1}, PDI = 1.03, Polymer Laboratories).

Matrix assisted laser desorption ionization – time of flight (MALDI-TOF) mass spectroscopy was performed using an Applied Biosystems Voyager-DE STR BioSpectrometry workstation. The block copolymer was dissolved in THF and premixed with the matrix *trans*-3-indoleacrylic acid (IAA) dissolved in THF. The sample was analyzed in linear mode.

Synthesis of Hydroxyethyl Functionalized Polystyrene (HOEtPS) (2) via Anionic Polymerization. The anionic polymerization of styrene was carried out using standard high vacuum techniques. Styrene (10.18 g, 0.09 mol) and benzene (125 mL) were distilled into the reaction vessel and polymerization was initiated using *sec*-butyllithium (1.4 M solution in hexane, 1.45 mL, 2.04 mmol). Polymerization was allowed to proceed for a period of 14 h at room temperature (r.t.). An aliquot (~5 mL) of the solution was then removed from the reactor, and terminated with MeOH (0.25 mL), in order to provide a sample of unfunctionalized PS for analysis. The remaining PSLi in benzene was cooled in

an ice bath, and EO (0.28 g, 6.4 mmol, 3-4 equivs) was distilled into the solution. The mixture was stirred for 30 min, after which MeOH (0.83 mL, 2.0 mmol, ~10 equivs) was added. After 30 min the solvent was removed under reduced pressure. The sample was dissolved in THF (40 mL) and traces of MeOH were removed by azeotropic distillation. The solvent was removed under reduced pressure, and the sample was dried for 24 h in vacuo at 50 °C. Yield = 10.11 g, ~100%. The volumes of benzene solvent used in the polymerization reaction, and the volume of solution collected from the polymerization vessel in order to provide a sample of MeOH terminated PS, were not measured with a high degree of precision. Theoretical maximum and therefore percentage yields of the PS are not highly accurate as a result. Target M_n: 5000 g mol^{-1}. THF GPC: M_n = 5900 g mol^{-1}, PDI = 1.09. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.3 ($C_6\mathbf{H_5}$ of PS), 3.38–3.10 ($CH_2C\mathbf{H_2}OH$), 2.4–1.7 (C**H** of PS), 1.7-1.24 (C$\mathbf{H_2}$ of PS), 1.24-0.5 (***sec*-Bu**). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.8-145.0, (*ipso*-C of $\mathbf{C_6}H_5$ of PS), 129-127.2, 126.4–125.4 ($\mathbf{C_6}H_5$ of PS), 61.2-60.8 ($CH_2\mathbf{C}H_2OH$), 47–41.35 (**C**H_2 of PS), 41.35–40.4 (**C**H of PS), 40.2–39.8, 39.6–39.0 (**C**H_2 of PS/**C**H of PS), 32.0-28.4, 20.1-18.4, 11.6–10.8 (all ***sec*-Bu**).

Recovery of MeOH Terminated Polystyrene. The solution of PS terminated with MeOH was precipitated into MeOH (40 mL). The polymer was filtered and dried in vacuo. Following this the product was twice reprecipitated from toluene (2.5 mL) into hexane (20 mL), filtered, and dried in vacuo. Yield = 0.48 g. Target M_n: 5000 g mol^{-1}. THF GPC: M_n = 5720 g mol^{-1}, PDI = 1.10. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.3 ($C_6\mathbf{H_5}$ of PS), 2.4–1.7 (C**H** of PS), 1.7-1.24 (C$\mathbf{H_2}$ of PS), 1.24-0.5 (***sec*-Bu**). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.8-145.0 (*ipso*-C of $\mathbf{C_6}H_5$ of PS), 143-142 (terminal CH_2 *ipso*-C of $\mathbf{C_6}H_5$ of PS), 129-127.2, 126.4–125.4 ($\mathbf{C_6}H_5$ of PS), 47.0–41.35 (**C**H_2 of PS), 41.35–40.4 (**C**H of PS), 40.2–40.0, 39.5, 38.5–37.8 (**C**H_2 of PS/ **C**H of PS), 34.1-33.7 (terminal **C**H of PS), 32.0–28.4 (***sec*-Bu**), 20.1-18.4, 11.6–10.8 (all ***sec*-Bu**).

Synthesis of PS Macromonomer (3) using a K Mirror. 4-VBC was passed through a short column of basic alumina, dried and degassed over CaH_2, and purified by vacuum distillation immediately prior to use.

Hydroxyethyl functionalized PS **2** (HOEtPS, M_n = 5900 g mol^{-1}, 5.00 g, 0.9 mmol) was dissolved in THF (100 mL) under an atmosphere of Ar in a bulb equipped with a septum. Potassium (0.2 g, 5.1 mmol, 5 equivs) was added to a second bulb under a stream of N_2 and placed under vacuum for 30 min, before being heated to form a mirror. The polymer solution was then added slowly to the K mirror to deprotonate the HOEtPS and the two were allowed to remain in contact for 24 h. (The solution was decanted into the first bulb and back again several times, to ensure the complete destruction of any trace amounts of protic impurities that might otherwise result in un-reacted HOEtPS contaminating the macromonomer. After this period the THF solution of KOEtPS was then decanted back into the first bulb, and freshly distilled 4-VBC (0.14 mL, 1.0 mmol, 1.2 equivs) was injected through the septum. The mixture was stirred for 24 h, after which air was admitted into the bulb. The polymer solution was diluted with THF (100 mL) and passed through a column of celite, in order to remove Li and K salts. It was then concentrated under vacuum (to 25 mL), precipitated into MeOH (200 mL), redissolved in toluene (25 mL) and reprecipitated into MeOH (200 mL) twice, to ensure the complete removal of unreacted 4-VBC. The sample was filtered and dried in vacuo at r.t overnight. Yield = 4.78 g, 94%. THF GPC: M_n = 6040 g mol^{-1}, PDI = 1.10. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4-7.2 (O-CH_2-C_6**H$_4$**CH=CH_2), 7.4–6.3 (C_6**H$_5$** of PS), 5.76–5.64 (C**H**H=CH-C_6H_4), 5.24–5.16 (CH**H**=CH-C_6H_4), 4.36-4.12 (O-C**H$_2$**-C_6H_4-CH=CH_2), 3.34–2.98 (PS-CH_2C**H$_2$**O-$CH_2C_6H_4$CH=CH_2), 2.4–1.7 (C**H** of PS), 1.7-1.24 (C**H$_2$** of PS), 1.24-0.5 (***sec*-Bu**). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.8-145.0 (ipso - **C$_6$**H$_5$ of PS), 139.0-138.8, 137 (CH_2=CH-**C$_6$**H$_4$), 136.9 (CH_2=**C**H-C_6H_4), 129-127.2, 126.4–125.4 (**C$_6$**H$_5$ of PS, CH_2=CH-**C$_6$**H$_4$), 113.8-113.6 (**C**H$_2$=CH-C_6H_4), 72.6 (O-C**H$_2$**-C_6H_4-CH=CH_2), 68.5 (PS-CH_2C**H$_2$**O-CH_2-C_6H_4-CH=CH_2), 47–41.35 (**C**H$_2$ of PS), 41.35–40.4 (**C**H of PS), 40.2–39.8, 39.6–39.0 (**C**H$_2$ of PS/**C**H of PS), 32.0-28.4, 20.1-18.4, 11.6–10.8 (all ***sec*-Bu**).

Synthesis of PS Macromonomer (3) using NaH. Hydroxyethyl functionalized PS **2** (HOEtPS, 2.00 g, 0.2 mmol, PS M_n: 10 600 g mol^{-1}) and NaH (0.05 g, 1.9 mmol, 10 equivs) were added to a 2-neck 100 mL round bottom flask equipped with a magnetic follower and stoppered with rubber septa. The flask was maintained under an atmosphere of N_2. The polymer was dissolved by the addition of dry THF (20

mL) to the flask with agitation, following which 15-Crown-5 (0.38 mL, 1.9 mmol, 10 equivs) was added to the suspension. 4-VBC (0.27 mL, 1.9 mmol), which had been dried over fused $CaCl_2$ for two hours at 4 °C, was then passed through a short column of basic alumina and immediately added to the reaction. Periodically samples (1 mL) were removed through the septa using a syringe, and were precipitated into IPA (10 mL), filtered, washed with IPA (5 x 10 mL), and dried briefly under vacuum. Conversion of the starting material HOEtPS to macromonomer was monitored using ^{1}H NMR by following the disappearance of the signal observed at 3.38–3.10 ppm ($CH_2C\mathbf{H_2}OH$) and the emergence of the signal in the macromonomer at approximately 3.34–2.98 ppm (PS-$CH_2C\mathbf{H_2}O$-$CH_2C_6H_4$-$CH{=}CH_2$). The reaction was complete within 48 h. Residual NaH was destroyed by the addition of a few drops of MeOH. The polymer solution (16 mL) was then precipitated into MeOH (160 mL), filtered and washed with MeOH (5 x 40 mL) before being dried in vacuo. The macromonomer was purified by passing a dilute solution (DCM) of it through a short (1.5 cm) column of celite, eluting the polymer with more DCM (total 100 mL), and removing the solvent under vacuum. The polymer was reprecipitated twice from toluene (10 mL) into MeOH (100 mL); the solid produced was isolated by filtration, washed with MeOH (5 x 40 mL), and dried in vacuo at r.t. overnight. Yield = 1.40 g (86%, based on polymer left after reaction monitoring). Analytical data was identical to that from macromonomers synthesized using a K mirror.

Synthesis of a PS Ruthenium Macroinitiator (5). In a nitrogen-filled glovebox (M.Braun), PS macromonomer (M_n = 10 700 g mol^{-1}, 0.500 g, 5 x 10^{-2} mmol) was dissolved in C_6H_6 (3.0 mL) and placed in an ampule. $RuCl_2(=CHEt)(PCy_3)_2$ (0.044 g, 6 x 10^{-2} mmol, 1.2 equivs) was dissolved in C_6H_6 (2.00 mL) in another ampule. Both ampules were transferred to a vacuum line and placed under Ar. A flow of Ar was then passed through the agitated solution of ruthenium initiator while the solution of PS macromonomer was slowly introduced via a cannula. Upon complete addition the reaction was stirred for 1 h. The solution was reduced to half its original volume under vacuum and added drop-wise to vigorously stirred, degassed hexane (chilled to -78 ^{o}C, 25 mL) producing a purple-red precipitate. The mixture was then filtered and washed thoroughly with chilled hexane (3 x 30 mL) using standard cannula techniques. The solid product, the macroinitiator, was dried at room temperature and in vacuo

($2x10^{-6}$ mbar) overnight, redissolved in C_6H_6 (2 mL) in the glovebox and precipitated into hexane (20 mL (chilled to -78 ^oC to ensure the product precipitated as a powdery solid) and washed with hexane as previously described, to ensure complete removal of any unreacted $RuCl_2(=CHEt)(PCy_3)_2$. Yield = 0.280 g, 53%. The macroinitiator was fully characterized by NMR using the aid of existing assignments for the PEO macroinitiator[8] and $RuCl_2(=CHPh)(PCy_3)_2$.[15] ^1H NMR (C_6D_6, 500 MHz): δ 20.56 (s, Ru=C**H**), 8.71 (br, *o*-**H** of C_6H_4 relative to Ru=CH), 7.3-6.4 (C_6**H**$_5$ of PS and residual H in C_6D_6), 3.92-3.70 (PS-CH_2CH_2O-C**H**$_2$-C_6H_4-CH=Ru), 3.24–2.96 (PS-CH_2C**H**$_2$O-CH_2-C_6H_4-CH=Ru), 2.90 (m, P(C_6**H**$_{11}$)$_3$), 2.60-1.10 (C**H** and C**H**$_2$ of PS, all m, P(C_6**H**$_{11}$)$_3$), 1.1–0.42 (***sec*-Bu**). ^{13}C NMR (C_6D_6, 126 MHz, v.s C_6D_6): δ 153.35 (s, *ipso*-C of **C**$_6$H$_4$ relative to Ru=CH), 146.8-145.0 (*ipso*-C of **C**$_6$H$_5$ of PS), 141.32 (s, *p*-**C** of **C**$_6$H$_4$ relative to Ru=CH), 131.47 (s, *o*/*m*-**C** of **C**$_6$H$_4$ relative to Ru=CH), 129.4–127.8, (**C**$_6$H$_5$ of PS, *o*/*m*-**C** of **C**$_6$H$_4$ relative to Ru=CH and **C**$_6$D$_6$), 127.0–126.4 (**C**$_6$H$_5$ of PS), 73.46 (br, PS-CH_2CH_2O-**C**H_2-C_6H_4-CH=Ru), 69.28 (br, PS-CH_2**C**H_2O-CH_2-C_6H_4-CH=Ru), 48.0–42.0 (**C**H_2 of PS), 42.0–41.2 (**C**H of PS), 32.03 (*pseudo*-t, *ipso*-C of P(**C**$_6$H$_{11}$)$_3$), 30.76 (s, *m*-C of P(**C**$_6$H$_{11}$)$_3$), 28.75 (*pseudo*-t, *o*-C of P(**C**$_6$H$_{11}$)$_3$), 27.55 (s, *p*-C of P(**C**$_6$H$_{11}$)$_3$). ^{31}P NMR (C_6D_6, 202 MHz): δ 37.14 (s, **P**Cy_3).

A typical block copolymer preparation. Synthesis of Poly(Styrene)-*block*-(*exo*-*N*-Phenylbutylbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxyimide). PS [Degree of Polymerization (DP) = 100] - PNB A (DP = 500). All ROMP reactions were performed in a nitrogen-filled glovebox (M.Braun) in screw top vials. *exo*-*N*-Phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (Monomer **A**, 0.259 g, 0.9 mmol) was dissolved in CH_2Cl_2 (10 mL). This solution was added to a stirred solution of a ruthenium PS macroinitiator (0.020 g, 2 x 10^{-3} mmol, PS macromonomer M_n = 10 500 g mol^{-1}, DP = ~ 100) dissolved in CH_2Cl_2 (0.5 mL). After 5 h the living polymer was terminated by the addition of ethyl vinyl ether (0.1 mL, 1.1 mmol) under a stream of N_2. The solution was stirred for a further 1 h, after which it was concentrated to approximately 3.0 mL using a stream of N_2 and precipitated into MeOH (30 mL) with vigorous agitation. The resulting precipitate was recovered by filtration, washed with MeOH and dried in vacuo at r.t. overnight. Yield = 0.243 g, 88%. Target M_n: 158

400 g mol^{-1}. THF GPC: M_n = 151 200 g mol^{-1}, PDI = 1.09. The block copolymer was fully characterized by NMR using the numbering scheme shown in Figure 1. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.9 (**H$_{15-17,20-22}$**), 6.9–6.3 (**H$_{20/21/22}$**), 5.78-5.66 (brm, *trans* **H$_{5,6}$**), 5.56-5.45 (*cis* **H$_{5,6}$**), 3.50–3.36 (brm, **H$_{10}$**), 3.23-3.10 (brm, *cis* **H$_{2,3}$**), 3.07-2.87 (brm, *trans* **H$_{2,3}$**), 2.69 (brm, *cis* **H$_{1,4}$**), 2.62 (brm, *trans* **H$_{1,4 \text{ and } 13}$**), 2.4–1.7 (**H$_{7/7',18}$**), 1.7-1.24 (**H$_{7/7',11,12,23}$**). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 178.56–178.2 (**C$_{8,9}$**), 146.8-145.0 (**C$_{19}$**), 142.53/142.44 (**C$_{14}$**), 133.6 (*trans* **C$_{5,6}$**), 132.4–131.8 (*cis* **C$_{5,6}$**), 129-127.4 (**C$_{15,16,20/21/22}$**), 126.4–125.4 (all **C$_{17,20/21/22}$**), 52.72 (*cis* **C$_{2,3}$**), 51.43-51.14 (*trans*, **C$_{2,3}$**), 47.0–40.4 (**C$_{1,4,7,18,23}$**), 38.51/38.35 (**C$_{10}$**) 35.54/35.50 (**C$_{13}$**), 29.03/28.96, 27.52/27.49 (**C$_{11,12}$**).

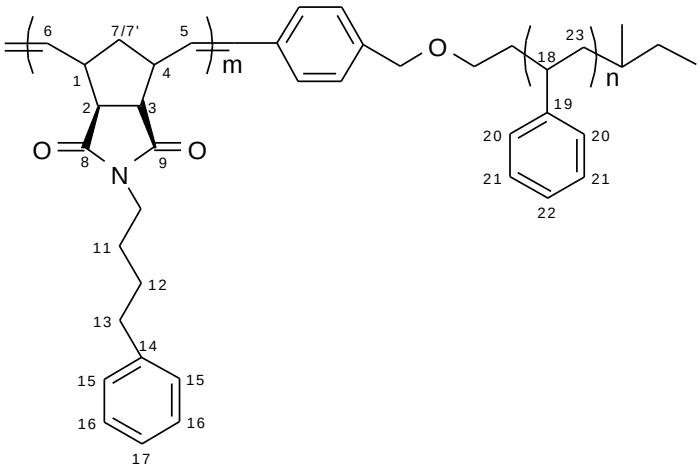


Figure 1.

Block copolymers of varying compositions of PS and a total of 3 different ROMP monomers were prepared in an analogous manner, by varying the M_n of the PS block, and ratio of ROMP monomer to macroinitiator together with the time allowed for complete consumption of the ROMP monomer. In the case of monomer **A** 1 h was allowed for a block copolymer with ROMP block of DP = 100, in the case of monomer **B** a time of 24 h, and in the case of monomer **C** a time of 1h. The reaction times were increased in proportion with increases in the target DP of the ROMP block.

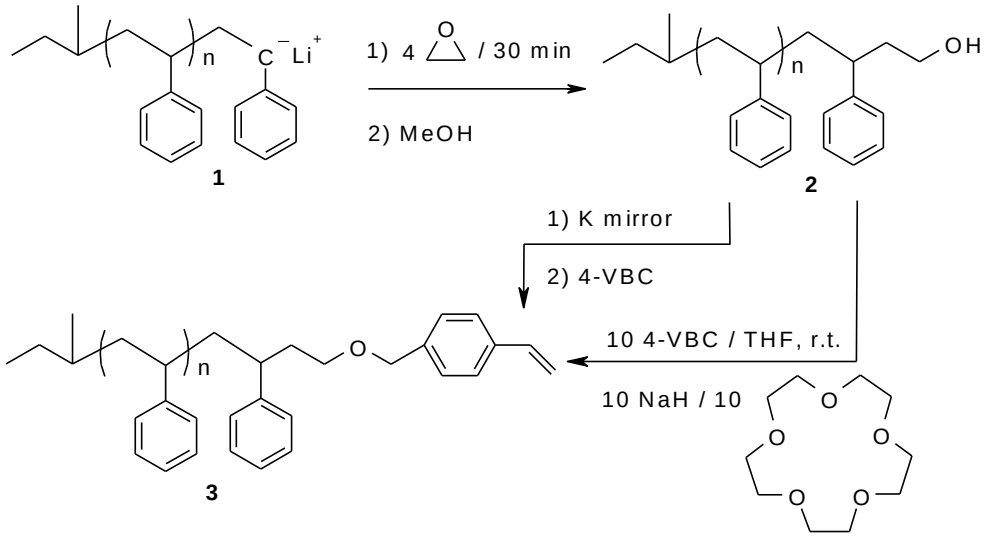
Results and Discussion

The synthesis of a range of block copolymers containing a PS and a polynorbornene (PNB) block has been achieved by the conversion of lithium initiated living anionic polymerization into ruthenium catalyzed ROMP. The living anionic polymerization of styrene was initiated using *sec*-butyllithium, in order to synthesize the block copolymers it is necessary to quantitatively convert the living PS into macromonomers by end-functionalizing them with 4-VBC. The greater reactivity of the carbanions of living PS, compared with those of the oxyanions present on living PEO chains, complicates their functionalization.[3] The addition of 4-VBC to PSLi using the reaction conditions used to functionalize the PEO macromonomers[8] results in vinyl addition, as well as the desired S_N2 reaction with the chloromethyl group.[9] The S_N2 reaction with the benzyl halide is faster than the reaction with the vinyl group, but even by increasing the molar excess of 4-VBC (with respect to the chain ends) to 8.25 : 1, only 50% of the resulting product mixture is the desired macromonomer, the other major component being a dimer of polystyrene.[9] Asami et al. have developed a method for the direct functionalization of PS-Li using 4-VBC.[9] This required specially designed equipment in which the living PS-Li in C_6H_6 was pre-mixed with THF, creating a highly solvated ion-pair, and hence increasing the reactivity of PS-Li towards the benzylic halides relative to the vinyl group. However, in order to yield a product free of PS dimer the 4-VBC must be used in the form of a dilute solution in THF, and the method of combination of the two requires precise control; the PS-Li solution being added dropwise to the 4-VBC solution at 0 °C to ensure an excess of the benzyl halide with respect to living chain ends at all times. Whilst it has been reported that no significant termination of PSLi by THF occurs over the lifetime of the experiment when 20% (v/v) THF is used in cyclohexane,[16] a general problem with the use of THF in organolithium synthesis is metallation of the solvent[17,18] - even PSLi itself is unstable in pure THF.[19,20] It could thus be anticipated that in some cases functionalization of polymers with 4-VBC would be accompanied by a significant amount of side reaction with THF. A method was thus sought that would avoid the design and use of new and complicated equipment, and which would not require extensive optimization in order to generate macromonomers from different anionic polymerizations. It is anticipated that such a

method might form the basis for a general strategy that could be used for the synthesis of macromonomers from other lithium initiated anionic polymerization reactions.

The approach that was adopted in this research to the synthesis of PS macromonomers was to use Quirk's method[21] to functionalize living PS (**1**) with ethylene oxide (EO) to synthesize hydroxyethylated PS (**2**) (Scheme 1). The macromonomer (**3**) was then synthesized by a coupling reaction, between **2** and 4-VBC, based on the Williamson ether synthesis.

Scheme 1. Synthesis of Polystyrene Macromonomers.



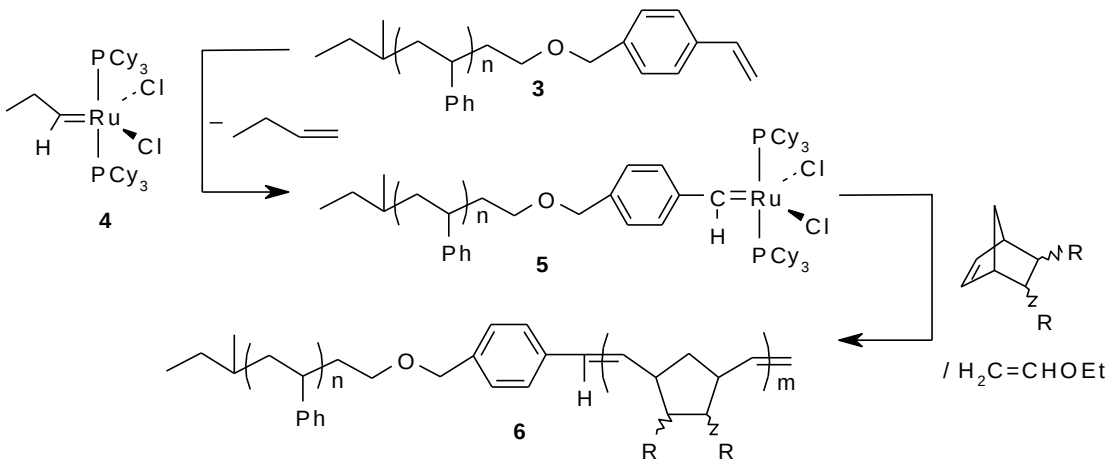
The reaction of polymeric organolithium compounds with EO has been shown to be a useful method for the hydroxyl functionalization of many polymers synthesized via an anionic polymerization mechanism.[21-24] In the case of PS (and polybutadiene) the reaction is well-characterized and leads to quantitative hydroxylation.[25,26] Reaction of PS-Li (**1**) with EO yields polymeric oxyanion chain ends, which aggregate strongly in solution.[25] This aggregation inhibits propagation of EO resulting in the introduction of a single EO monomer unit. Oligomerization of EO can occur however with increased reaction times and concentrations of EO. The lithium alkoxide end group was protonated with N_2 sparged MeOH to yield **2**. Study of **2** via ^{1}H NMR spectroscopy indicated the presence of a single broad peak at 3.38–3.10 ppm corresponding to a single terminal methylene group adjacent to the hydroxyl group, no evidence of the extra signals between 3 and 4 ppm that would result from the ether linkage

formed via oligomerization were observed.[25]. Oligomerization is not expected to present a problem for the synthesis of macromonomers as the oligomeric product would be functionalized with a hydroxyl group, however the data suggests it did not occur to any detectable degree using our reaction conditions. Comparison of the integration values of the peak at 3.38-3.10 ppm corresponding to the CH_2OH methylene group with that from the aromatic phenyl protons of the PS polymer chain at 7.4–6.3 ppm confirmed that the reaction was virtually quantative. In all cases a sample of PSLi was withdrawn and terminated with MeOH prior to the addition of EO, and used for the determination of M_n of the polymer using GPC.

The conversion of the hydroxyl functionalized PS (**2**) into PS macromonomer (**3**) was achieved using a Williamson coupling reaction with 4-VBC, and was attempted successfully by two different routes. Firstly the hydroxyl group of **2** was deprotonated using a K mirror to yield a potassium alkoxide salt, which was then reacted with 4-VBC to form **3**. In a second approach the methodology of Aspinall et al.,[27] originally developed to allow the conversion of hindered alcohols into ethers at room temperature, was adapted for the synthesis of **3**. In this case the hydroxyl functionalized PS **2** was combined with 4-VBC, NaH, and 15-crown-5 and left stirring under dry N_2 until reaction was complete (48 h). Whilst the latter reaction was slower than the first method (K mirror), it needed less rigorous purification of 4-VBC and exclusion of moisture, and was catalyzed by a milder base. This could prove particularly useful when adapting the described methodology, for polymers containing functionalities that are sensitive to nucleophilic attack. In each case the product of the functionalization reaction was analyzed by NMR spectroscopy. The spectra of the products from both routes were identical as expected, indicating the quantitative conversion of **2** into **3** via both approaches.

The functionalized PS macromonomers **3** were used as precursors to ruthenium PS macroinitiators for ROMP (Scheme 2, **5**), which were used to initiate the ROMP of norbornene derivatives, resulting in the synthesis of a series of block copolymers (**6**).

Scheme 2. Synthesis of Poly(Styrene–Norbornene) Block Copolymers.[a]



[a] Cy = Cyclohexyl.

The synthesis of the ruthenium PS macroinitiators **5** was achieved by an analogous alkylidene exchange reaction to that used to convert PEO macromonomers into PEO ruthenium macrointiators.[8] The alkylidene exchange reaction of PS macromonomer **3** with ruthenium propylidene initiator $RuCl_2(=CHC_2H_5)(PCy_3)_2$ (**4**), resulted in the synthesis of **5**. This reaction is an equilibrium process and thus the 1-butene side product must be removed in order to effect complete conversion of macromonomer **3** to macroinitiator **5**.[8] The solution containing the ruthenium initiator was purged with argon prior to and during the reaction, to ensure complete removal of the 1-butene by-product, which is a gas at room temperature. The success of the reaction can be monitored by the absence of the peaks from the vinyl functionality of the macromonomer **3** in the ^{1}H NMR spectrum of the final product, as well as changes in the alkylidene region. The triplet due to the alkylidene proton of the propylidene initiator **4** at 19.62 ppm (**a**, Figure 2) disappears and is replaced by a resonance due to the alkylidene proton of the macroinitiator **5** at 20.58 ppm (**b**, Figure 2), which is similar to that observed for the ruthenium benzylidene initiator.[8]

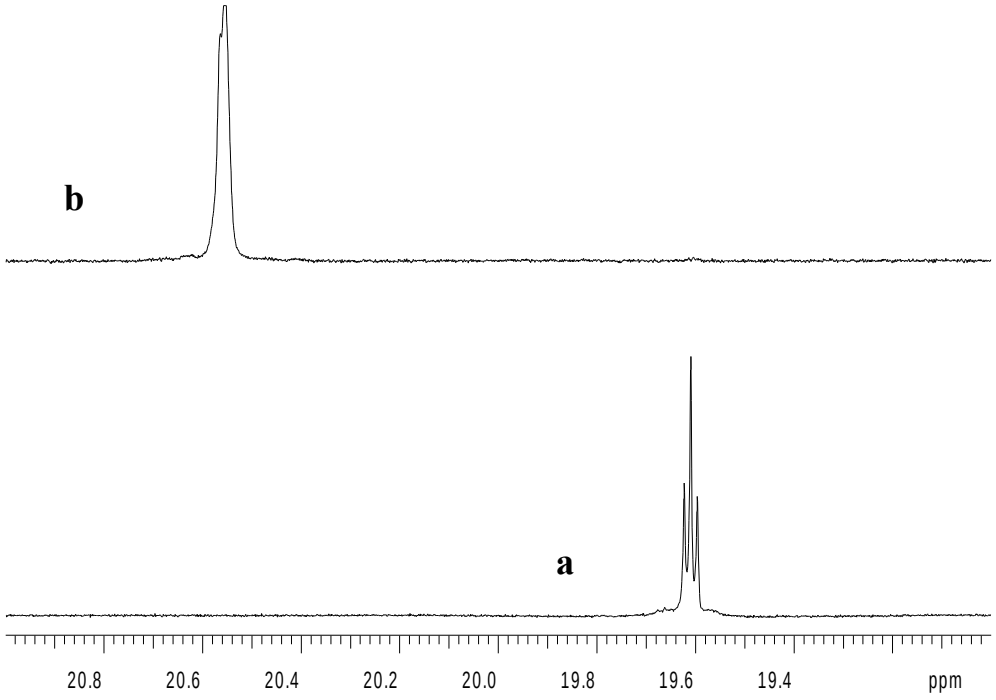


Figure 2.

A series of PS macroinitiators were synthesized with the number average molecular weight (M_n) of PS (THF GPC) ranging from 2850 to 10 500 g mol^{-1}. The macroinitiators were subsequently used in the synthesis of block copolymers of styrene with NBE derivatives. Three different ROMP monomers were used for the synthesis of block copolymers (Figure 3).

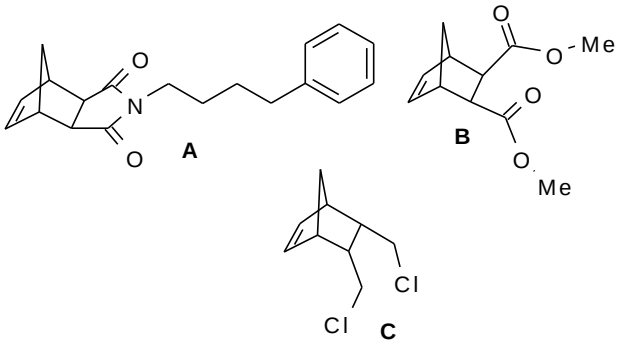


Figure 3.

A series of block copolymers were synthesized in which the composition was controlled by altering the ratios of monomer [M] to macroinitiator [MI]; [M]/[MI] = 100, 200, and 500. Consumption of

monomer was quantitative and in almost all cases the block copolymers possessed a narrow molecular weight distribution (PDI of 1.05-1.2). This suggests that as with the PEO macroinitiators, the PS macroinitiators are efficient initiators for the ROMP of the NBE derivatives investigated.

Table 1. Molecular Weight and Composition Data for a Series of Diblock Copolymers

Sample	PS Block[a]			ROMP Block		Block Copolymer			
	M_n g mol^{-1}	M_w g mol^{-1}	PDI	Monomer	DP	M_n/Pred[b] g mol^{-1}	M_n/GPC g mol^{-1}	PDI	M_n/NMR g mol^{-1}
1	2850	2900	1.02	**A**	100	32 500	29 700	1.16	32 600
2	5700	6300	1.10		100	35 400	32 700	1.10	34 100
3	10 500	11 100	1.06		100	40 200	38 400	1.07	43 100
4					200	69 700	68 300	1.07	68 700
5					500	158 400	151 200	1.09	159 000
6	2850	2900	1.02	**B**	100	24 000	15 600	1.15	23 900
7	5700	6300	1.10		100	26 900	20 800	1.09	26 200
8	10 500	11 100	1.06		100	31 700	23 100	1.05	31 000
9	5700	6300	1.10	**C**	100	25 000	23 100	1.17	24 900
10	10 500	11 100	1.06		100	29 800	22 600	1.24	30 900

a Determined by THF GPC. *b* Based on GPC measurements of the PS block.

The block copolymers were precipitated into MeOH, a non-solvent for both the PS and PNB blocks so that any PS homopolymer, if present, should be observed in the GPC chromatograms. A small peak was sometimes observed at an elution volume where the PS homopolymers would be expected (**a** in Figure 4). A shoulder was also observed at lower elution times, corresponding to approximately double the molecular weight of the block copolymers (**b** in Figure 4), which as with the PEO-PNB block copolymers is attributed to polymer-polymer coupling by dimerization of the living polymer after ROMP. Further work was conducted to examine the formation of this species, which was consistent with this idea, and is discussed in the supporting information.

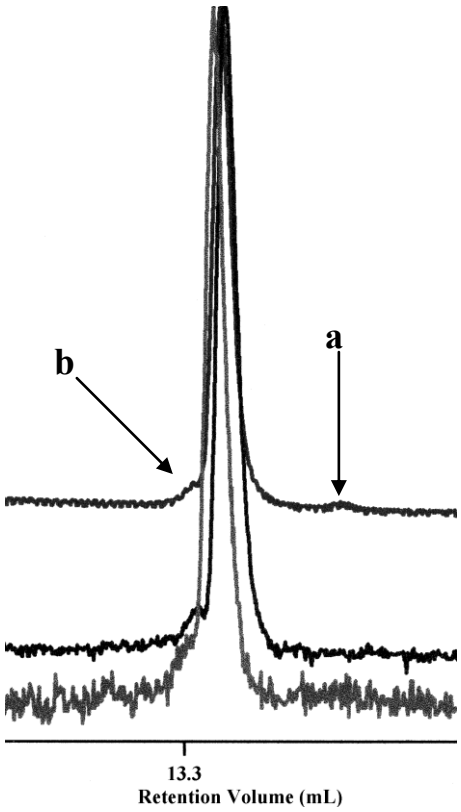


Figure 4.

The values of M_n for the block copolymers, calculated by GPC using triple detection (Table 1) are lower than those predicted by the stoichiometry of the reaction. The data obtained by triple detection GPC is based upon the parameters for PS measured in THF solution (e.g. refractive index [RI], specific refractive index increment [d*n*/d*c*], and intrinsic viscosity [η]), we would not therefore expect the values from GPC to be accurate. Homopolymers of all three NBE monomers were synthesized using benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$ using the same conditions that were used to polymerize the ROMP block of the copolymers. All three were studied by GPC using THF as the eluent; in all cases the calculated data for M_n were lower than the predicted values. For example a sample of homo-PNB **B** (predicted M_n: 21 050 g mol^{-1}, DP = 100) had a calculated value of 12 700 g mol^{-1} for M_n (PDI = 1.02).

The GPC analysis of the block copolymers is important in that it gives an accurate measure of the polydispersity of the copolymers. Previously reported methods for synthesizing block copolymers by combining well-defined ruthenium initiated ROMP and PS, have produced materials that possess a rather broad molecular weight distribution.[28,13] For instance the ROMP of norbornene derivatives

initiated by ruthenium initiators was used to create macroinitiators that initiated the ATRP of styrene, resulting in the synthesis of block copolymers of styrene with a PDI of 2.70.[29] The molecular weight distributions of the block copolymer synthesized with our methodology thus compare very favourably with PS-PNB block copolymers synthesized via other routes.

The ^{1}H NMR spectra of the PS-PNB block copolymers can be used to calculate a quantitative value for the molecular weight (M_n) of the block copolymers, as we know the M_n of the PS block from GPC. To calculate the ratio of PNB to PS blocks the integrals of a peak from each of the two polymer backbones must be compared. This allows the calculation of the DP of the PNB block, using the DP of the PS block of known M_n, and hence the M_n of the block copolymers. The calculation is discussed in detail in the supporting information. The values for M_n calculated by NMR are in good agreement with those predicted by the stoichiometry (Table 1).

The percentages of *cis* and *trans* vinylene units in the ROMP blocks of the PS-PNB block copolymers of NBE **A** and **C** were compared with those of the homo PNB polymers synthesized using $RuCl_2(=CHPh)(PCy_3)_2$, and the previously reported PEO-PNB block copolymers.[8] In the case of PNB **A**, the results were calculated by comparison of the integration values of the ^{1}H NMR resonances of the vinylene protons of *cis* and *trans* units, which fall at 5.54-5.47 and 5.76-5.70 ppm respectively, and in PNB **C** the *cis* and *trans* bridgehead methine protons at 3.11 and 2.83 ppm were used. The percentage of *cis* vinylene units was determined to be in the region of 20% for all of the PNB homopolymers and PS-PNB block copolymers studied, which is typical of polymers synthesized using $RuCl_2(=CHPh)(PCy_3)_2$.[30]

PS-PNB diblock copolymer sample 3 (Table 1) was subjected to MALDI analysis (Figure 5).

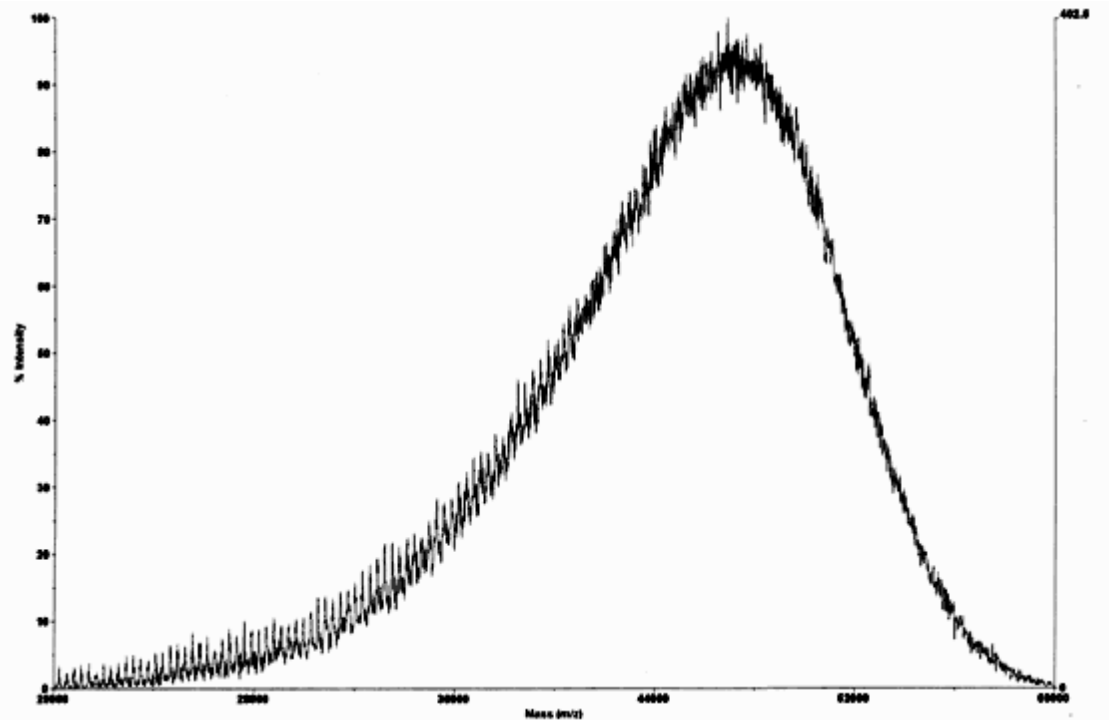
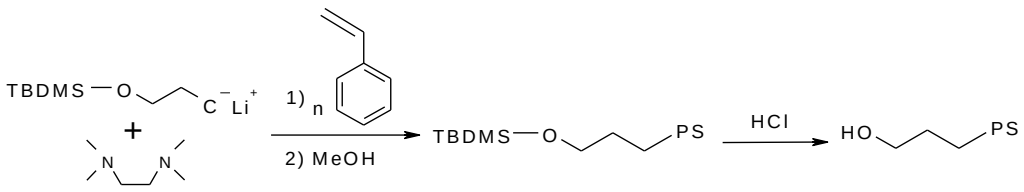


Figure 5

The preferential ionization of one polymer block in block copolymers can be observed, reducing the accuracy of the molecular weight data.[31,32] However a value of 44 300 g mol^{-1} for M_n was calculated from the MALDI data, in good agreement with the predicted 40 200 g mol^{-1}. The resolution in the spectrum was insufficient to see individual macromolecules, probably due to the high molecular weight of the block copolymer.

Synthesis of a PS Macromonomer using an Initiator Containing a *tert*-Butyldimethylsilyl Ether (TBDMSO) Protected Hydroxyl Group. An alternative and facile approach to the synthesis of PS macromonomers was also recently developed. Instead of end-functionalizing the living chain end with EO after polymerization, the hydroxyl functionality was incorporated into the polymer chains via the use of an anionic initiator with the hydroxyl group protected by a TBDMSO group (Scheme 3).

Scheme 3. Synthesis of Hydroxyl Functionalised PS using a TBDMSO Functionalized Initiator.



After deprotection of the hydroxyl group, the polymer was coupled with 4-VBC using the methodology depicted in Scheme 1, resulting in the synthesis of a PS macromonomer. Full details of the synthesis and characterization of this PS macromonomer are given in the supporting information.

Conclusions

A methodology for the synthesis of well-defined block copolymers, where one block is synthesized via anionic polymerization, initiated using alkyllithium compounds, and subsequently, the second block via ruthenium initiated ROMP, has been developed. The methodology was demonstrated by the synthesis of macromonomers and subsequently block copolymers from living (PS). This was achieved by means of an end functionalization reaction with ethylene oxide, and conversion of the hydroxyl functionalized product into macromonomer via a Williamson ether synthesis reaction involving the PS-OH and 4-VBC. Alkylidene exchange reactions between the PS macromonomer and ruthenium propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ resulted in the synthesis of ruthenium PS macroinitiators for ROMP. Addition of norbornene derivatives to the macroinitiators resulted in the synthesis of a range of block copolymers that possessed narrow molecular weight distributions, and contained little or no homo-polymer.

Acknowledgments. We are grateful for assistance with NMR analysis from Dr Alan M. Kenwright and his team and for the MALDI spectra provided by Dr David Parker, all from the Department of Chemistry, University of Durham, UK. We thank the UK EPSRC for financial support.

Supporting Information Available: Calculation of M_n of block copolymers using ^1H NMR. Study of polymer-polymer coupling during ROMP. Synthesis of PS Macromonomer using TBDMSO functionalized initiator. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure Captions

Figure 1. Numbering scheme for NMR assignments of poly(styrene)-block-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide)

Figure 2. Comparison of the ^{1}H NMR analysis of the ruthenium propylidene initiator and the PS macroinitiator formed as a product of the alkylidene exchange reaction between the propylidene initiator and PS macromonomer (C_6D_6). **a** Ruthenium propylidene initiator and **b** PS Ruthenium macroinitiator.

Figure 3. Norbornene derivatives that were copolymerized with styrene.

Figure 4. Triple detection GPC chromatogram of PS-PNB diblock copolymer sample 6 prepared from PS and monomer **B**. M_n = 15 600 g mol^{-1}, PDI = 1.10, contaminated with a trace of PS homopolymer (**a**) of M_n = 2900 g mol^{-1}, PDI = 1.02. Refractive Index (top), viscosity (middle) and light scattering (bottom) detector responses shown.

Figure 5. MALDI spectrum of poly(styrene)-*block*-(*exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide). Sample PS-PNB 3, Table 1. M_n: 44 300 g mol^{-1}, PDI: 1.02

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BLOCK COPOLYMERS BY THE CONVERSION OF LIVING LITHIUM INITIATED ANIONIC POLYMERIZATION INTO LIVING RUTHENIUM ROMP

Thomas C. Castle, Ezat Khosravi and Lian R. Hutchings